

Use of Synchrotron Reflectance Infrared Spectromicroscopy as a Rapid, Direct, Non-Destructive Method for the Study of Inks on Paper

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INTRODUCTION

The analysis of inks and the paper to which they are applied is of great interest to a broad spectrum of science. From the historian and archaeologist to the forensic scientist, an understanding of ink-paper interactions is essential to the understanding of the ink and its subsequent changes upon application to paper. Determining chemical and other details of ink in a signature, for example, can be an exceedingly difficult task. Modern ballpoint writing inks are frequently mixtures of ink vehicles (used to dissolve the dyes or disperse pigments), dyes and/or pigments, various resins and polymers (to control the viscosity of the ink and to serve as “fillers”), acidic materials (frequently fatty acids that function as lubricants), and surface-active agents. Additionally, other organics may be used to control corrosion or improve solubility of the dyes and pigments.

From the moment that a writing ink is applied to paper material, both the chemical composition of the ink and the ink/paper interface begin to undergo changes. Various physical and chemical processes occur, including the evaporation of solvents and other volatile compounds, polymerization, oxidation, cross-linking, and, in some cases, paper corrosion. These processes can also include those that are effected by external factors such as heat and light, with possible chemical reactions being photolytically induced. Other interactions with the paper are possible.

In the present work, the use of synchrotron radiation-based infrared (SR-FTIR) spectromicroscopy offers a powerful, non-destructive method for the study and identification of inks on paper and the comparison of them to one another without the need for chemical separations and related laboratory work. Also, this method allows for a detailed analysis without the inherent destruction of the ink samples on the paper by more commonly used technique.

EXPERIMENTAL

The ink/paper combinations were analyzed using infrared Beamline 1.4.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. All spectra were obtained using collimated synchrotron light directed into a Nicolet Magna 760 FT-IR bench. The deconvolution work of several of the parent ink infrared spectra was performed using the Nicolet software in conjunction with search libraries from Sigma-Aldrich that are copyright-assigned to Nicolet. All samples were analyzed by collecting a minimum of 256 scans in the mid-IR range (4000-400 cm⁻¹). Residual water and carbon dioxide were subtracted where appropriate, and baselines were normalized using the correction routines present in the software.

To prepare samples for infrared study, ink was applied to paper strips (~2.5 cm x 5 cm). The paper strips were placed on the infrared microscope sample holder and were measured in reflectance mode. The paper used was measured to have a transmittance of < 1% throughout the mid-IR, so reflection-absorption (IR passing through the paper, reflecting off the microscope stage, and then passing back through the paper) can be ruled out. The measurements obtained were therefore dominated by specular reflectance, with some diffuse reflected light collected as well. Also, some ink component compounds were identified by taking the spectra of the ink that had been directly applied to a silver coated microscope slide [Kevley Technologies, Chesterland, OH

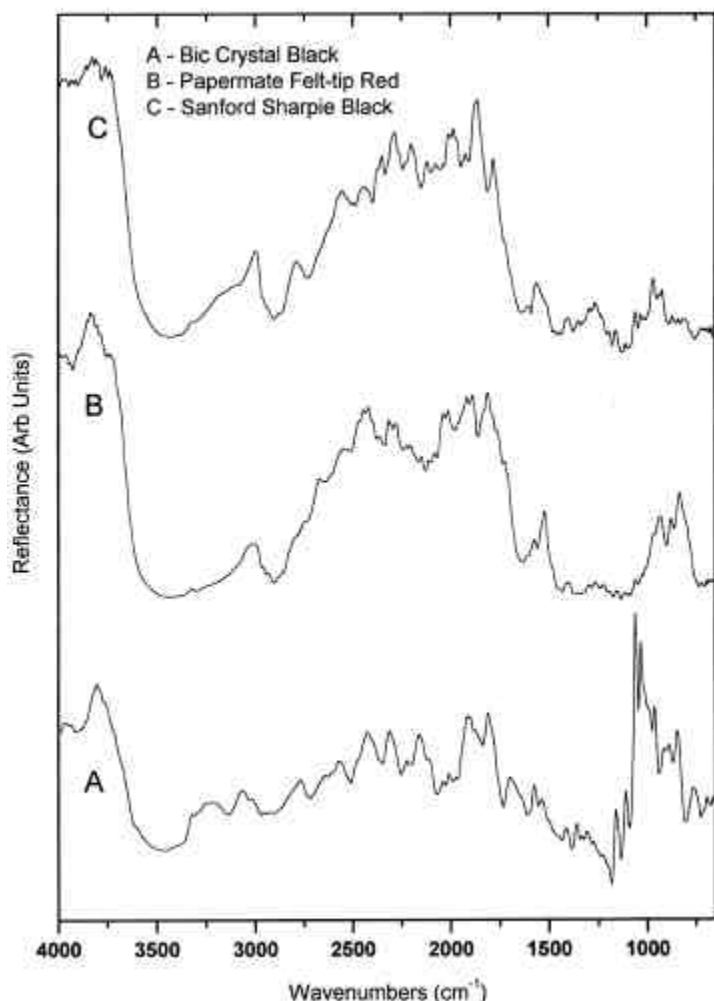


Figure 1. Infrared spectra of a) a commercial black ink, b) a commercial red ink, and c) another commercial black ink all on the same Whatman 3MM Chr chromatography paper.

RESULTS AND DISCUSSION

As mentioned above, the chemistry of inks in commercial pens is highly complex, and as a result, the infrared spectra of the inks tend to be quite complicated because of the overlap of many of the vibrational bands from the different constituents. Figure 1 shows the infrared spectra of three typical commercial inks on a high-purity chromatographic paper. All of the spectra exhibit bands which are common to many compounds that are typically used in ink formulations. One readily assignable area of the spectrum is the 2900-3000 cm^{-1} region associated with the $\nu(\text{C-H})$ stretch for aliphatic hydrocarbons. The $\sim 3500 \text{ cm}^{-1}$ region is associated with the $\nu(\text{OH})$ stretch of water and alcohol solvents that are typical for many ink systems. More complicated, however, is the $\sim 800\text{--}1700 \text{ cm}^{-1}$ "fingerprint region" in which many of the ink constituents' infrared spectra overlap with one another. In yet another region (1700-3500 cm^{-1}) for blue, black, and red inks such as shown in Figure 1, the spectra are seen to be equally complex. All of these regions contain multiple vibrational bands such

as C=C, C=N, C-O, C=O, C-N, C-S, S-O, ring modes (both aromatic and aliphatic), and combination bands from the dozens of compounds that constitute each ink.

The use of synchrotron-based FT-infrared microspectroscopy described herein for the study of inks and their interactions with paper affords several advantages over other experimental and spectroscopic approaches. First, it is a direct method with no necessity for any pre-chemical separations such as chromatography. Second, the technique represents a method for obtaining a molecular fingerprint of different inks that make them easily and readily distinguishable. Third, it offers an extremely high lateral spatial resolution of less than 10 μm , much smaller than any line made on paper by normal ball point or fountain pens and much smaller than the "worst case" situation for examining ink samples on paper ("...probably the true worst case is the examination of a single dot..."). Fourth, the sensitivity of the synchrotron-based infrared technique is 200 times greater than a regular FT-infrared instrument for a 10 μm spot size, thus making it possible to see spectroscopic detail in some instances that would be missed by traditional spectrometers. Fifth, because of the mapping capability relative to the spatial resolution of the synchrotron spectromicroscopic technique, it is possible to study infrared spectroscopic profiles of the actual line interfaces of the different inks in a line or signature on paper (actually, spectroscopically seeing where one ink ends and another begins in the same signature, for example).

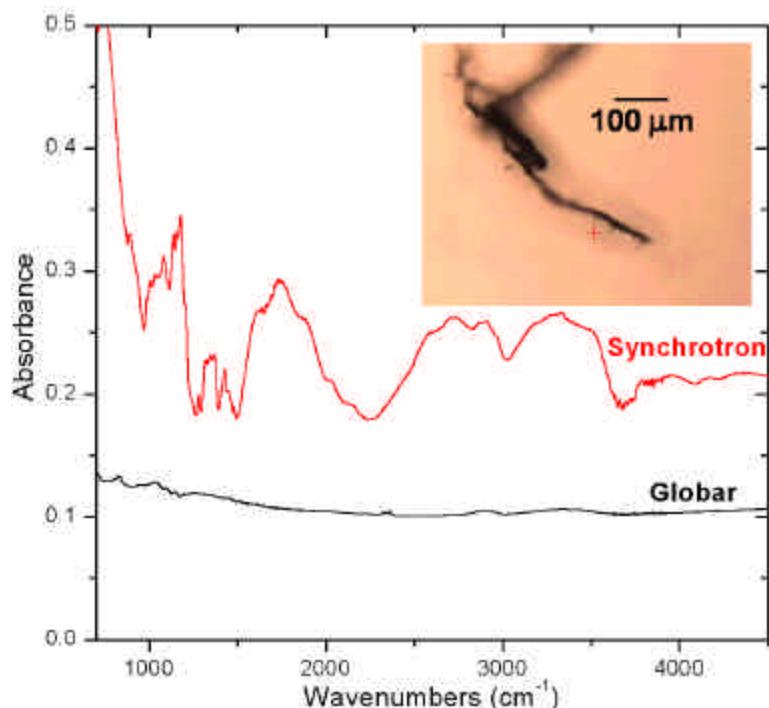


Figure 2. Infrared spectra of ink on a paper fiber using both synchrotron and Global™ infrared sources. The difference in the two spectra is due to the much greater brightness of the synchrotron impinging on the fiber.

fragmentary samples of ink on paper and for other ink/paper systems such as printed material.

Two comments should be made on the use of background subtraction. First, paper, even the same brand and type, is never pure or totally reproducible at the micron level. Paper batches are processed from different pulp sources blended together for the final product. Thus, there is a very high probability that a point analysis on the same sheet of paper may differ slightly. Second, when one microscopically examines ink on paper from a pen applied under normal writing conditions, one sees both paper and ink, not just an area of paper covered totally by the ink. The ratio of the ink-to-paper area being studied in a several micron area may vary. In any rigorous study of ink/paper combinations, an investigator should take a sampling of locations on the ink/paper line so as to get a more complete and truer spectromicroscopic picture of the sample of interest.

CONCLUSION

High resolution synchrotron infrared spectromicroscopy has potential for the direct facile and rapid comparative identification of writing inks. The technique can be used for the direct analyses of inks on paper without mechanically damaging the ink and paper or having to chemically extract or separate the ink. This method should be useful in other areas of studying ink, such as both qualitative and quantitative analysis of the ink components, verification of the identical nature of several inks, and the relative determination of the age of the ink.

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The issue of sensitivity and resolution as advantages to using synchrotron-based FTIR spectromicroscopy over traditional stand-alone infrared instrumentation for the study of ink on paper is dramatically illustrated in Figure 2. The inset photograph shows ink on a paper fiber being studied using both a synchrotron infrared source on Beamline 1.4.3 at the ALS and a Global™ infrared source. The two spectra shown were taken using the two different infrared sources represent an ink spot on the paper fiber of ~10 microns, and they were taken using the same number of scans. The superior sensitivity and resolution of the synchrotron-based approach shown in Figure 2 emphasizes the nearly unlimited possibilities for the use of the techniques for looking at very small,